High resolution Far Infrared Fourier Transform Spectroscopy of the NH_2 Radical

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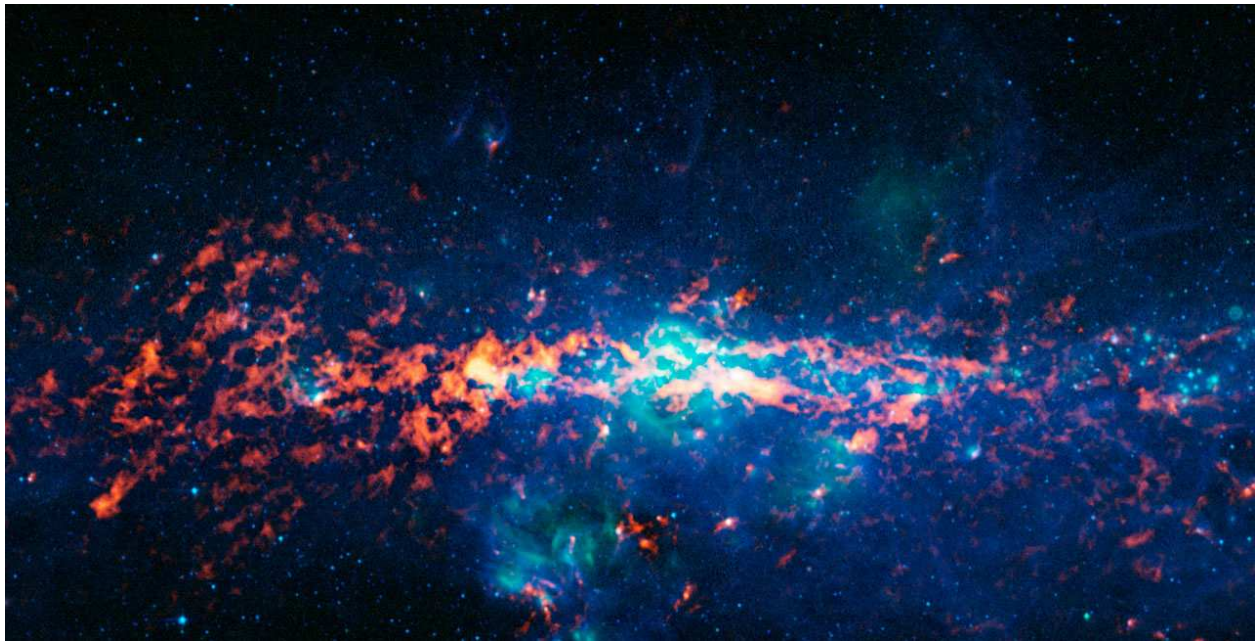
SOLEIL synchrotron - AILES beamline

66^{th} International Symposium on Molecular Spectroscopy

Astrophysical Background



ESO/APEX & MSX/IPAC/NASA

- 1^{st} detection towards SgrB2

Van Dishoek et al., *Astrophys. J.* **416** (1993)

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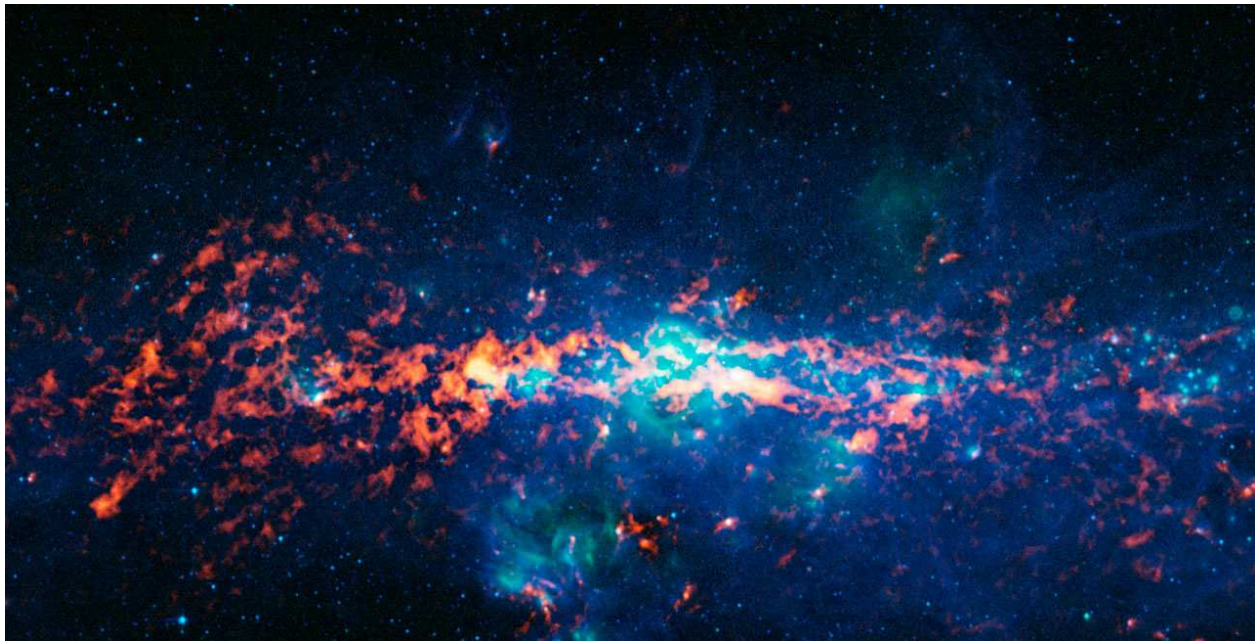

ESO/APEX & MSX/IPAC/NASA

- 1^{st} detection towards SgrB2

  Van Dishoek et al., *Astrophys. J.* **416** (1993)

- Recently detected by Herschel (HIFI) towards G10.6-0.4 (W31)

  Persson et al., *A&A* **521** (2010)

State of the Art

NH_2: extensively studied from the sub-mm to the UV

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  - R=0.007 cm^{-1}
  - Absorption spectroscopy in the ground vibrational state
  - 200 pure rotational transitions reported (N_{max}=12)

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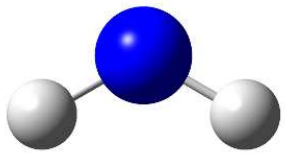
Objective

High resolution and high temperature

Spectroscopy of the NH_2 Radical

Electronic: fundamental state $\tilde{X}\ ^2B_1$

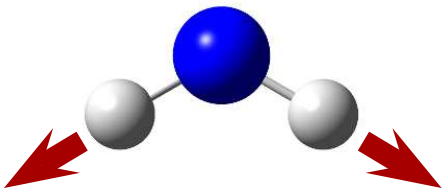


Spectroscopy of the NH_2 Radical

Electronic: fundamental state $\tilde{X}\ ^2B_1$

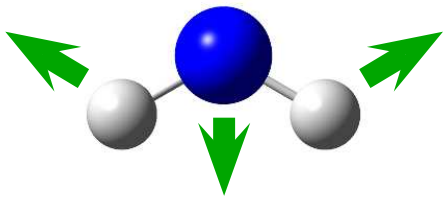
Vibrational: $3N - 6 = 3$ vibration modes (ν_1, ν_2, ν_3)

Symmetric stretching



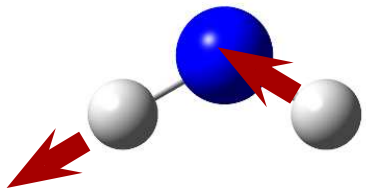
$\nu_1 = 3219 cm^{-1}$

Bending



$\nu_2 = 1497 cm^{-1}$

Asymmetric stretching



$\nu_3 = 3301 cm^{-1}$

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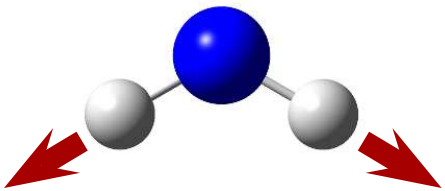

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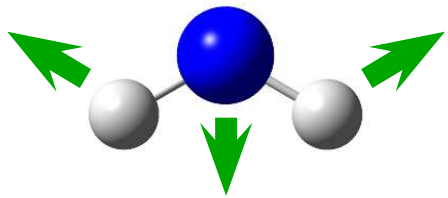

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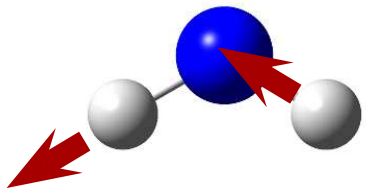

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Rotational: Asymmetric top rotor

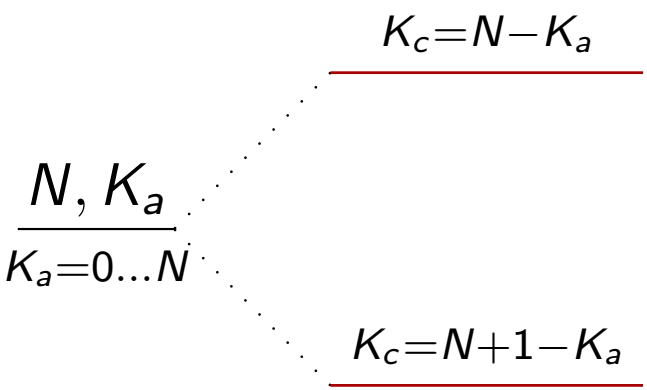
- Hund's case (b)
- Rotational quantum numbers: N, K_a, K_c
- (000), (010): b-type transitions

Rotational Structure

$$\frac{N, K_a}{K_a=0...N}$$

Rotational Structure

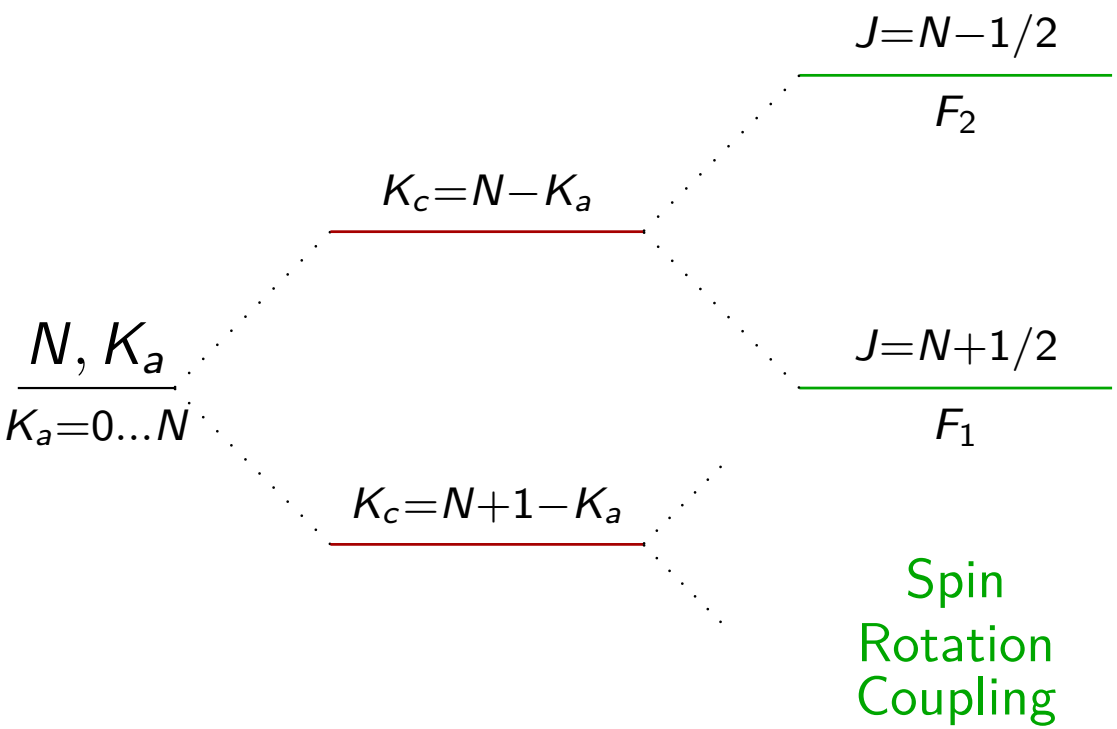
Asymmetric Splitting



$$K_a + K_c = N \text{ or } N + 1$$

Rotational Structure

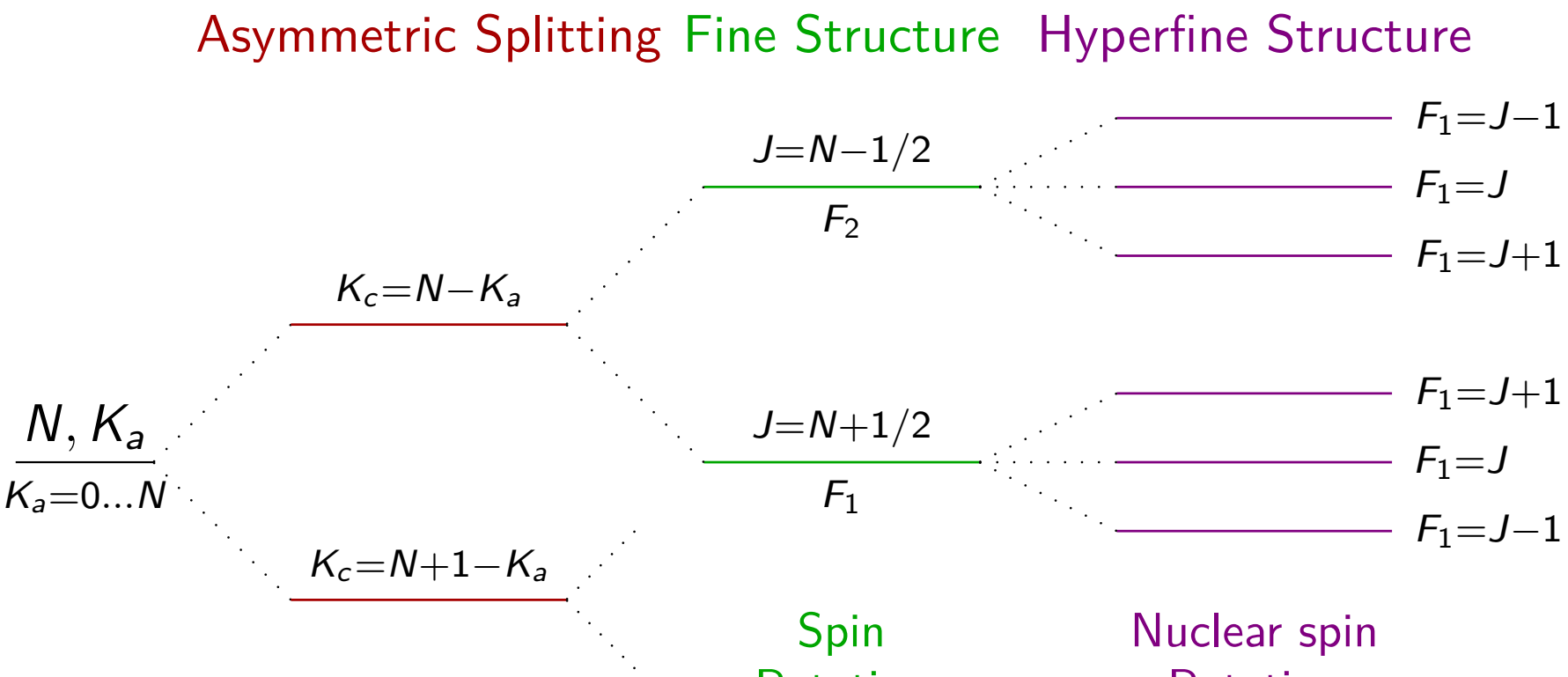
Asymmetric Splitting Fine Structure



$K_a + K_c =$
N or $N+1$

$\vec{J} = \vec{N} + \vec{S}$
S=1/2 ($^2B_1$)

Rotational Structure



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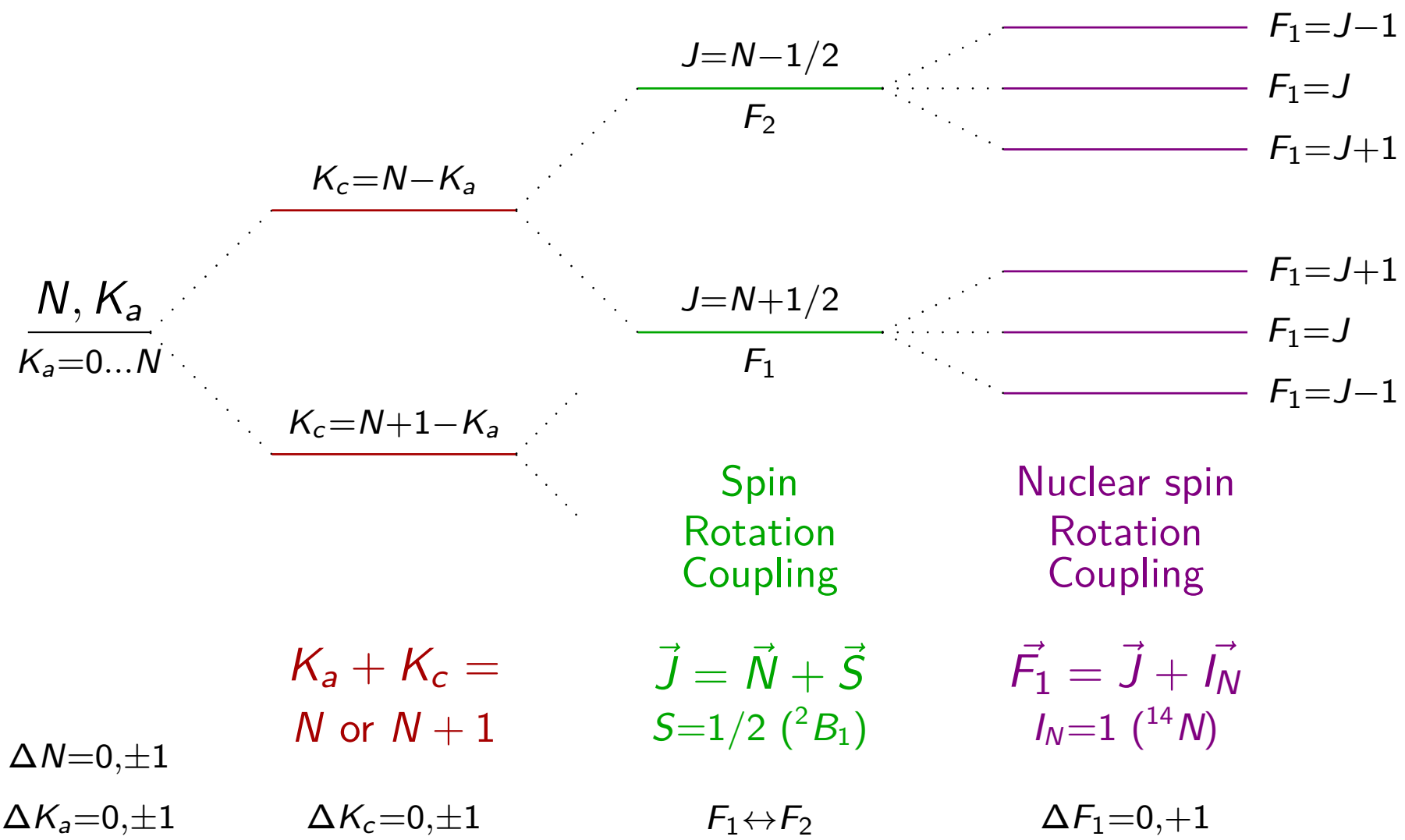
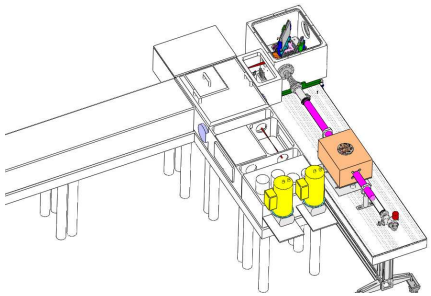
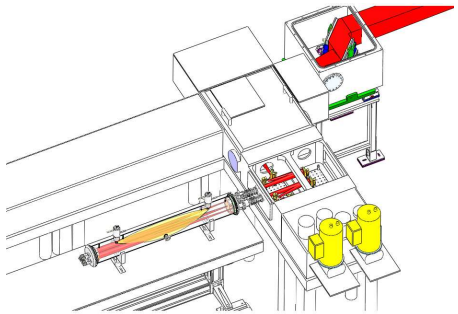


Experimental Set-ups

	Emission	Absorption
Interferometer	Bruker IFS 125	
Spectral range	15-700 cm^{-1}	
Precursor	NH_3	
Discharge	RF	DC
Power	1000 W	1-3 kV, 0.6-2 A
Pressure	~10 mbar	~0.1 mbar (+ 2 mbar He)
Light Source	plasma	SR
Resolution	$4{\cdot}10^{-3}$ cm^{-1}	$1{\cdot}10^{-3}$ cm^{-1}
Accuracy (l.p.)	$< 5{\cdot}10^{-4}$ cm^{-1} (12 MHz)	$< 1{\cdot}10^{-4}$ cm^{-1} (3 MHz)
Length	0.7 m	24 m
Rot. temp.	2500 K	300 K





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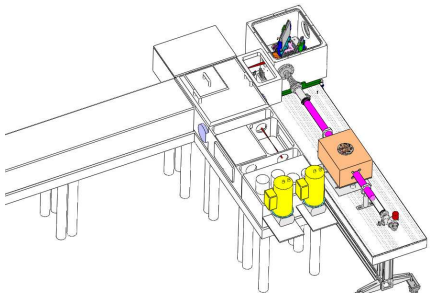

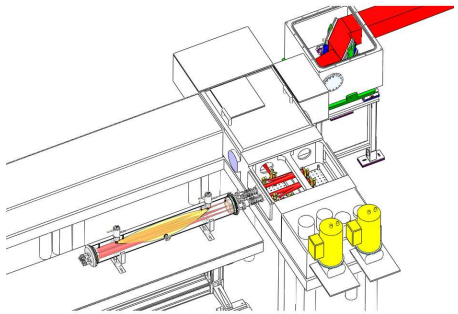

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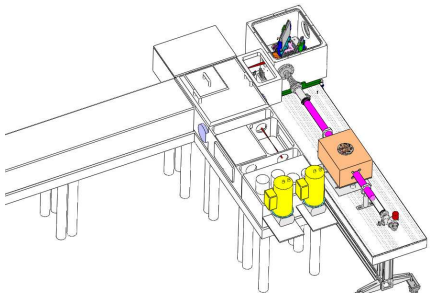

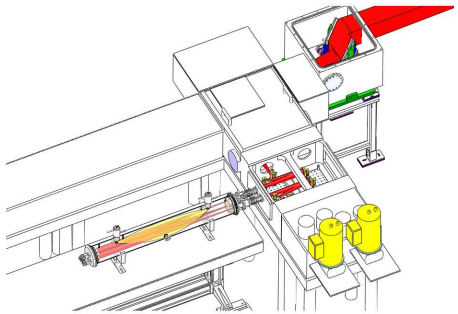

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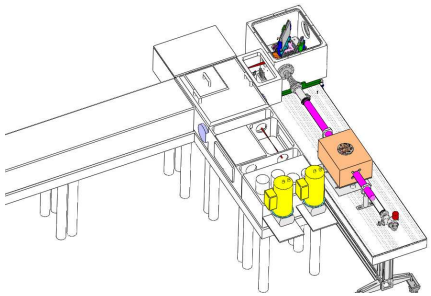

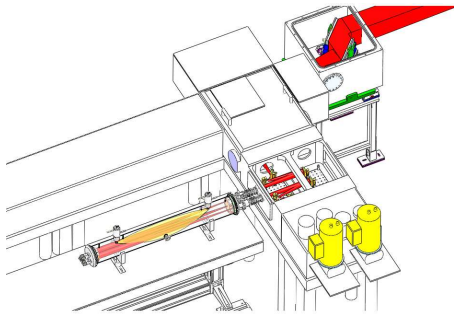

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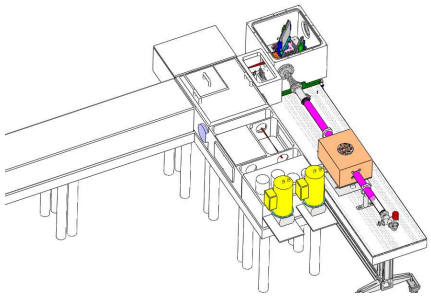
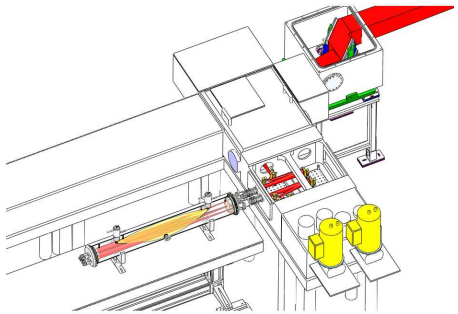
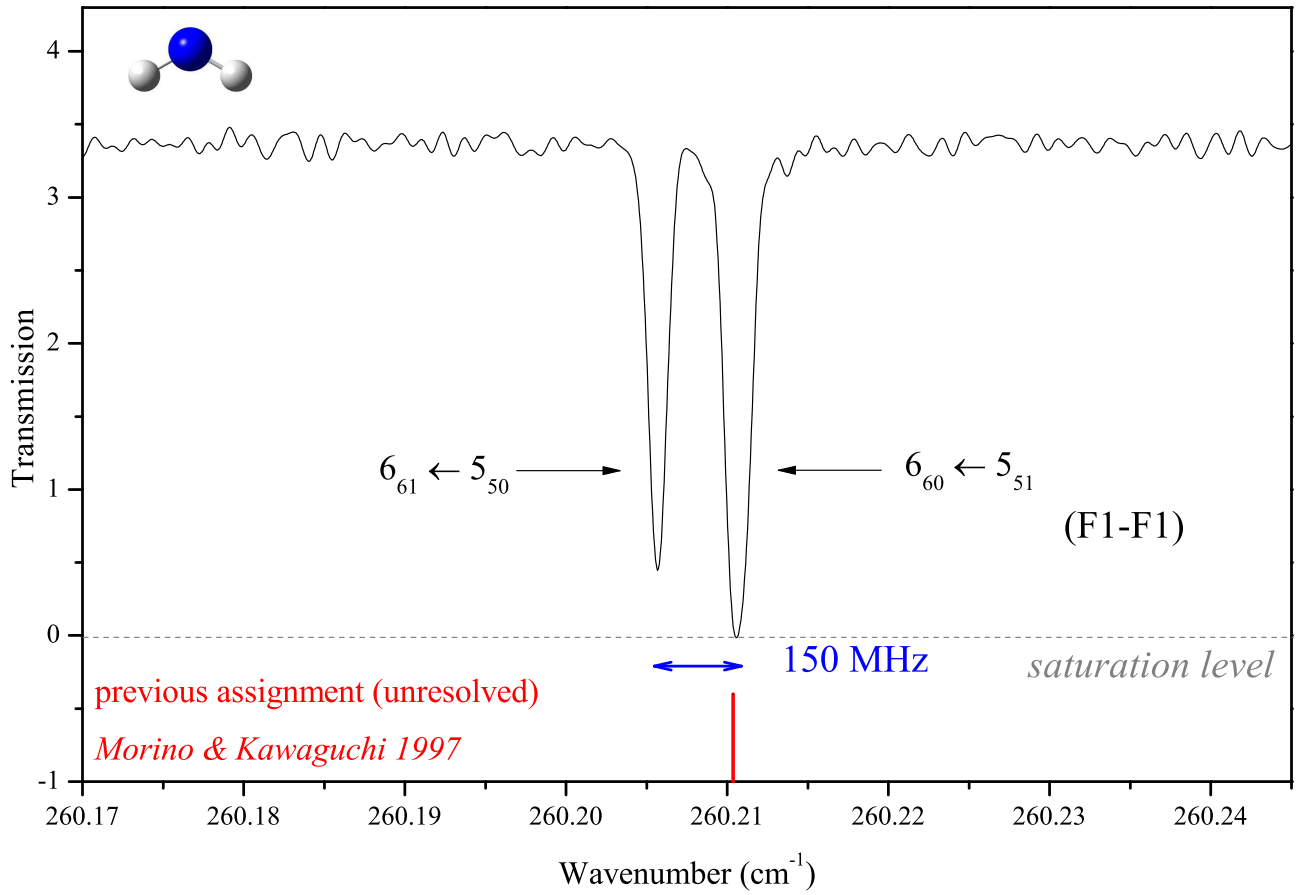


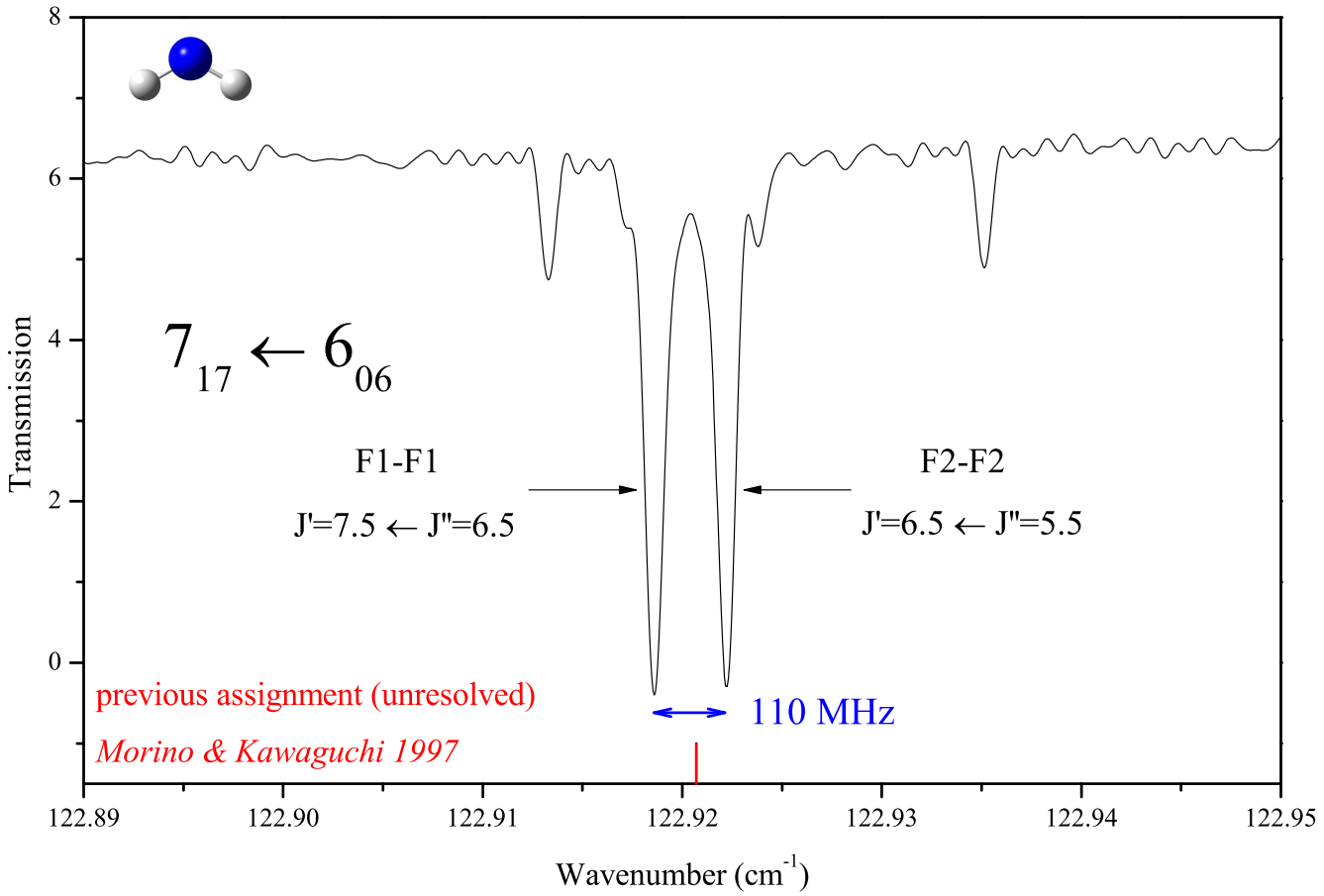


Resolution of the Asymmetric Splitting



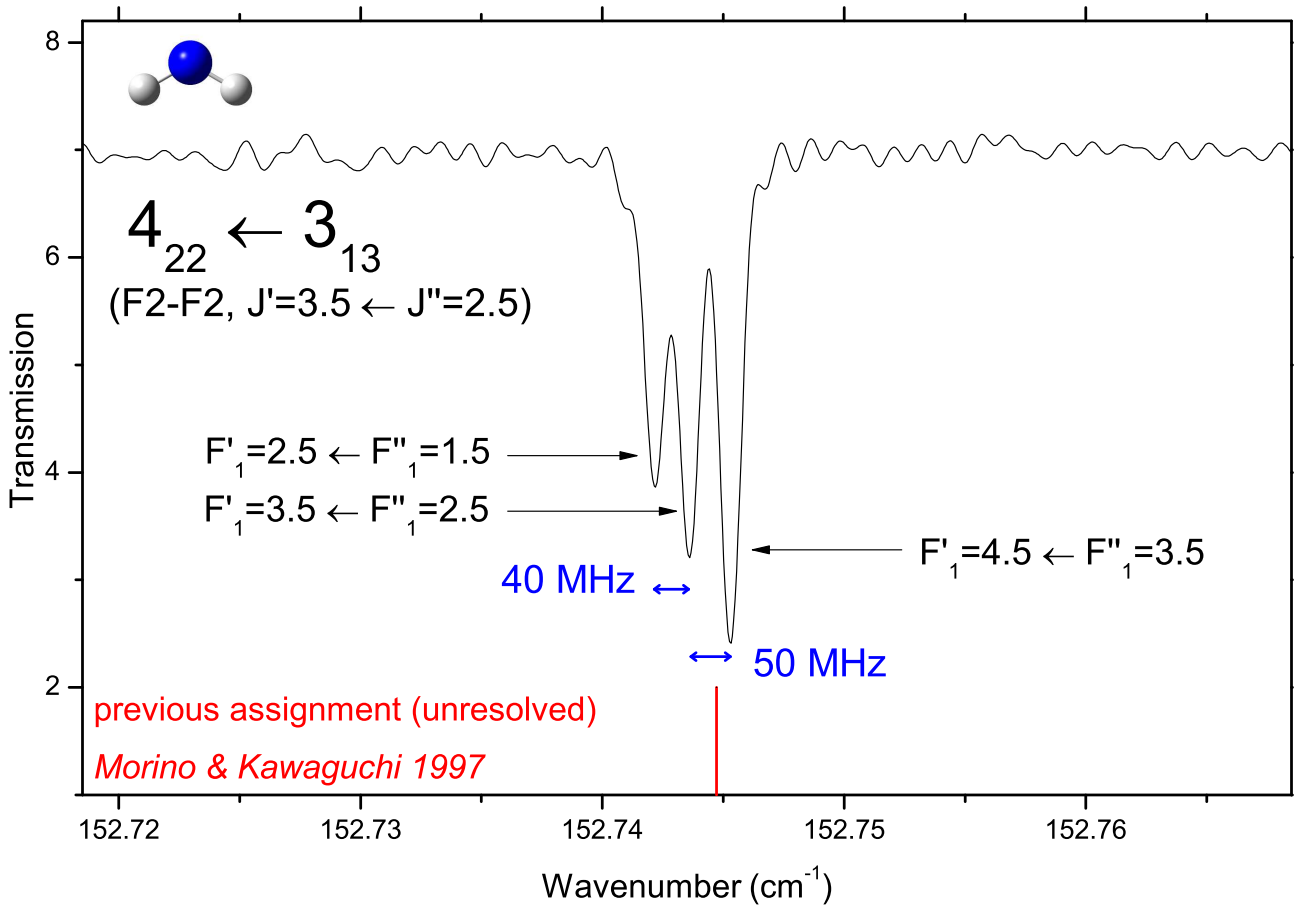
⋆ Absorption: Resolution of the asymmetric splitting for several new lines

Resolution of the Fine Structure



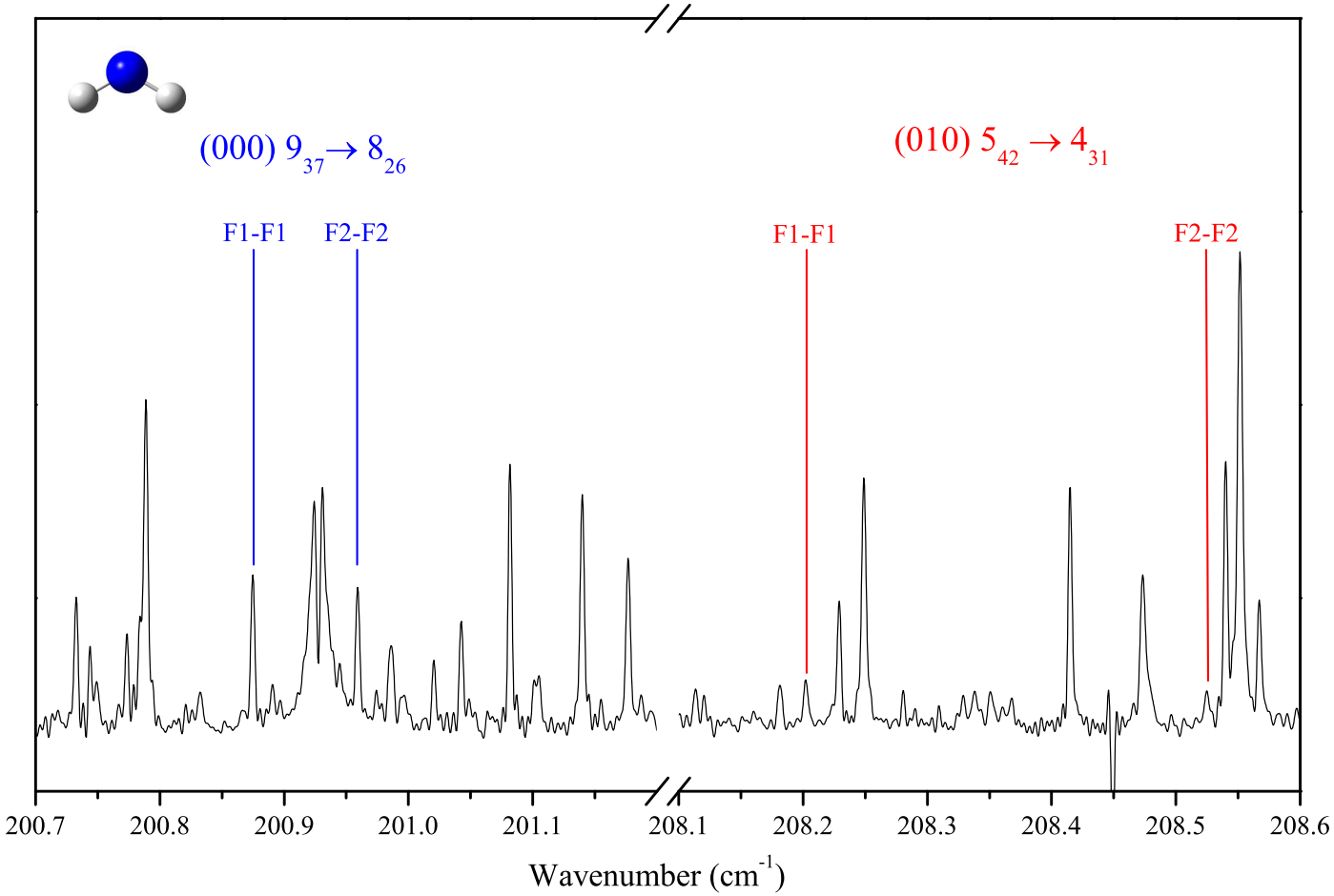
⋆ Absorption: Resolution of the fine structure for several new lines

Resolution of the ^{14}N Hyperfine Structure



⋆ Absorption: Resolution of the hyperfine structure for several new lines

Transition Involving Excited Energy Levels



⋆ Emission: Pure rotational transitions within (000) and $\nu_2 = 1$

Analysis (in progress)

- Use of the SPFIT/SPCAT suite

  Pickett et al., *J. Mol. Spect.* (1991)

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- Fit: pure rotational transitions within (000)
  - 684 previously reported transitions (0-2 THz $\sim$ 0-60 cm^{-1})

    Müller et al., *J. Mol. Spect.* **195** (1999)
  - $\sim$ 700 transitions observed at Soleil (20-700 cm^{-1})
  - Watson's A-reduced rotational Hamiltonian (I^r representation)
  - *IR RMS=1.1·10^{-3} cm^{-1}*
  - *RMS ERROR=1.58*

Fit

Fit 1

1191 lines (507 SOLEIL)
$N_{max} = 12$ ($K_a = 3$)
$K_{amax} = 9$ ($N = 9$)
73 parameters

IR RMS=0.00029 cm^{-1}
RMS ERROR=1.66

Fit 2

1365 lines (681 SOLEIL)
$N_{max} = 24$ ($K_a = 2$)
$K_{amax} = 9$ ($N = 13$)
86 parameters

IR RMS=0.00075 cm^{-1}
RMS ERROR=1.49

Fit 3

1385 lines (701 SOLEIL)
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- Light molecule: anormal centrifugal distorsion
- Renner-Teller effect

  Dressler & Ramsay, *Ph. Trans. Roy. Soc. London* **251** (1959)

- Unidentified transitions within (000) and (010)...

Rotational and Centrifugal Distortion Constants (MHz)

Parameter	Present	Müller et al.
A	710 302.011 4(104)	710 302.131 9(250)
B	388 289.646 8(113)	388 288.871 8(1491)
C	245 013.373 9(70)	245 013.954 4(1316)
Δ_K	659.752 41(262)	659.765 23(1561)
Δ_{NK}	-125.142 86(169)	-125.045 19(1631)
Δ_N	31.686 89(50)	31.664 38(428)
δ_K	29.751 6(38)	29.375 5(761)
δ_N	12.709 480(182)	12.701 85(208)
$\Phi_K \cdot 10^3$	1 991.01(34)	1 991.49(350)
$\Phi_{KN} \cdot 10^3$	-283.00(46)	-267.88(472)
$\Phi_{NK} \cdot 10^3$	-49.337(121)	-48.98(139)
$\Phi_N \cdot 10^3$	13.069 4(128)	12.518 3(1195)
$\phi_K \cdot 10^3$	539.25(37)	490.64(778)
$\phi_{NK} \cdot 10^3$	-15.742(53)	-18.655(1194)
$\phi_N \cdot 10^3$	6.506 1(59)	6.294 3(432)
$L_K \cdot 10^6$	-10 626.3(162)	-10 156.(278)
$L_{NNK} \cdot 10^6$	63.68(139)	70.39(1281)
$L_N \cdot 10^6$	-9.846(135)	-4.786(792)
$L_{NK} \cdot 10^6$	-1 045.4(66)	-736.9(1070)
$L_{KKN} \cdot 10^6$	3 882.4(179)	2 472.(290)
$l_K \cdot 10^6$	-4 646.3(161)	-2 501.(208)
$l_{KN} \cdot 10^6$	72.0(32)	44.3(432)
$l_{NK} \cdot 10^6$	3.889(256)	45.87(818)
$l_N \cdot 10^6$	-4.891(67)	-3.043(295)
$P_K \cdot 10^6$	44.16(41)	49.01(426)
$S_K \cdot 10^6$	-0.119 4(38)	-0.184 4(299)

Complement of NH_2 database

$\sim$ 500 new transitions identified in (000)

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- **Emission:**
  Observation of transitions involving excited energy levels
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  - (010) *(in progress)*

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- **Absorption:**
  High resolution and accuracy on line position
  - 1^{st} resolution of the rotational splitting for ~ 40 transitions // (asymmetric splitting (10), fine (10) and hyperfine (20) structures)
  - Improvement on line position accuracy for lines already reported ($< 3MHz / \sim 1 \cdot 10^{-4} cm^{-1}$)

Investigations on $^{14}N/^{15}N$ ratio

Objectives:

- Observation of pure rotational transitions of the $^{15}NH_2$ radical
- Identification on Herschel spectra ?

Collaboration:

- Astrophysicians: OBSPM, Evelyne Roueff; LRA, Maryvonne Gerin
- PhLAM: Laurent Margulès, Stéphane Bailleux
- ISMO-SOLEIL: Olivier Pirali, Marie-Aline Martin-Drumel

The THz Cosmos, June 24, Laurent Margulès (FA06, 10h27)